Evaluation of Enzymatic Breakers for the Reduction of Environmental and Health Hazards Associated with Hydraulic Fracturing Fluids

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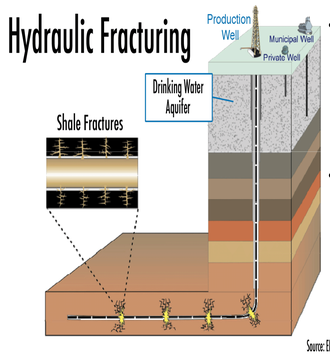
Introduction & Motivation

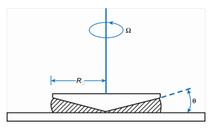


- High pressure fluids are used to obtain oil and natural gas that cannot be obtained by conventional methods.
- Fluid components give fluid desirable properties (e.g. polymer/crosslinker increase viscosity to fracture rocks, proppants hold open fissures, biocides kill bacteria).
- To increase flowback from the well (increasing yield), the polymer (guar) must be "broken" (degraded) to decrease its viscosity.
- A primary concern with fracking is its impact to health and the environment. Many fluid components known to be hazardous. There is a concern of the fluid contaminating drinking water.
- The goal was to identify and test alternative components for fracking fluids, specifically breakers, which are known to include some of the most hazardous components. Enzymes (benign to health and the environment) were proposed as alternatives.
- Two enzymes, β-mannanase and α-galactosidase, were compared against the industry-standard breaker, ammonium persulfate (strong oxidizer) through rheological and filter studies.
- Alternative components that meets or surpasses the performance of what is currently used may decrease the risks of fracking.

Experimental Methods

- Tests conducted with industry-standard fracking fluids: guar (0.5% wt. guar) and crosslinked guar (0.5% wt. guar, 0.25% wt. tetraborate).
- Breakers of varying identity and concentration were prepared: ammonium persulfate (APS; 0.01, 0.1% wt. final solution), mannanase (M; 0.01, 0.1 U/mL), galactosidase (G; 0.01, 0.1 U/mL), and a mixture of galactosidase and mannanase (G+M; 0.1 U/mL ea.).
- Fluids were treated with breakers at well conditions (50°C); reaction allowed to proceed for prescribed time (0, 15, 30, 45, 60 minutes).
- An Ares G2 Rheometer with cone and plate geometry was used to conduct frequency sweeps (0.1-100 rads/s) and steady shear rate sweeps (0.1-100 1/s) on fluids to determine the viscosity over time.
- Vacuum filtration was performed on broken samples (18 hr.) to evaluate each breaker's ability to degrade polymer to oligomers.
- Research also included analyses of breaker cost and health impact.

ARES G2 Rheometer

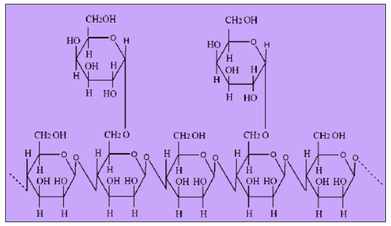


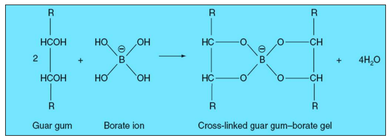
Parallel Plate Geometry

Filter Cake Vacuum Filtration

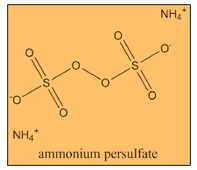
Chemical Species & Mechanisms

Guar and Crosslinked Guar

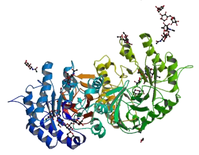




Breakers

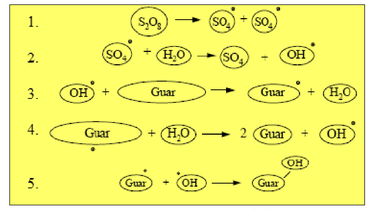


β-mannanase (M)

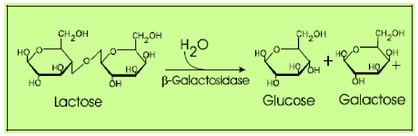


α-galactosidase (G)

Mechanisms

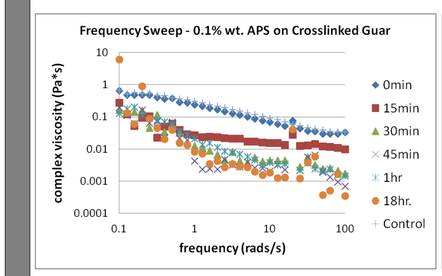


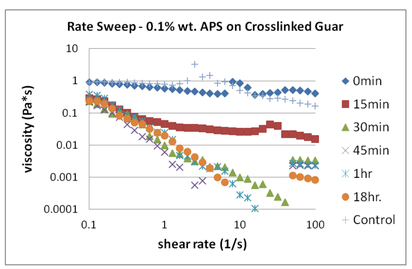
oxidative breaker (APS)

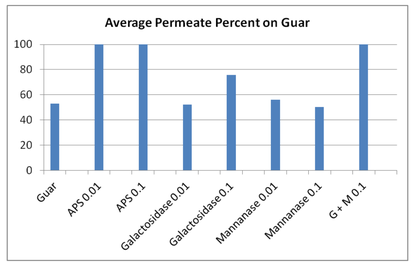


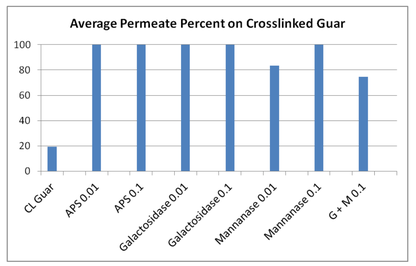
enzymatic breaker (M, G)

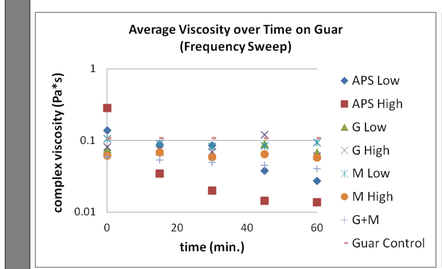
Experimental Results

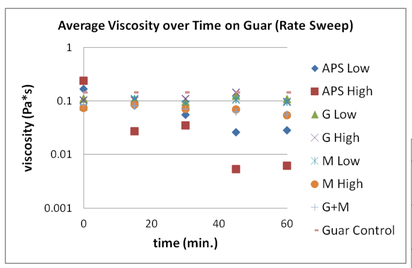


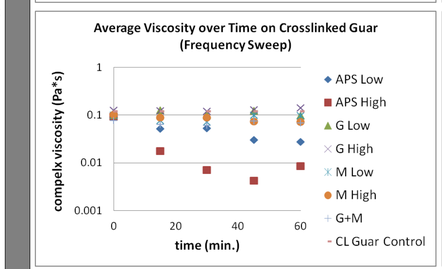


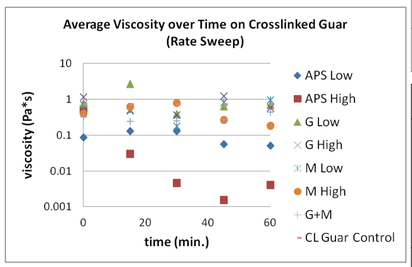












Breaker	Concentration	Cost ($/m³ fluid)
Ammonium Persulfate	0.01% wt.	0.072
	0.1% wt.	0.72
Mannanase	0.01 U/mL	0.005
	0.1 U/mL	0.05
Galactosidase	0.01 U/mL	0.35
	0.1 U/mL	3.50
Mannanase + Galactosidase	0.1 U/mL	3.55

Breaker	Effects
Ammonium Persulfate	acute toxin (oral LD_{50}: 700 mg/kg, dermal LD_{50}: 2000 mg/kg); eye, skin, and respiratory irritant; immunosuppressant; damage to gastrointestinal tract; acute and chronic aquatic toxin (LC_{50} for fish: 76 mg/L for 96 h)
Enzymes	benign to human health and the environment

Statistical Significance & Analyses

Filter-Degradation Model

Summary of Fit

RSquare	0.952585
RSquare Adj	0.932265
Root Mean Square Error	6.857275
Mean of Response	78.60645
Observations (or Sum Wgts)	31

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	19838.732	2204.30	46.8779
Error	21	987.467	47.02	Prob > F
C. Total	30	20826199		<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Fluid	1	1	179.572	3.8189	0.0641
Breaker	4	4	11470.455	60.9842	<.0001*
Fluid*Breaker	4	4	7136.348	37.9414	<.0001*

Tukey-Kramer:
- No enzyme same as APS
- Cross-effect of APS with fluids same as G with CL guar, M with CL guar, G+M with guar

Oscillatory Frequency Sweep Model

Summary of Fit

RSquare	0.677893
RSquare Adj	0.655245
Root Mean Square Error	0.020894
Mean of Response	0.071033
Observations (or Sum Wgts)	138

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	0.0117974	0.013066	29.9315
Error	128	0.0558770	0.000437	Prob > F
C. Total	137	0.1734755		<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Fluid	1	1	0.00747617	17.1258	<.0001*
Breaker	4	4	0.08891952	50.9189	<.0001*
Fluid*Breaker	4	4	0.01210849	6.9343	<.0001*

Tukey-Kramer:
- No enzyme same as APS
- Cross-effect of APS with fluids same as G+M with guar

Steady Shear Rate Sweep Model

Summary of Fit

RSquare	0.893995
RSquare Adj	0.885322
Root Mean Square Error	0.045868
Mean of Response	0.141525
Observations (or Sum Wgts)	120

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	1.9517403	0.216860	103.0763
Error	110	0.2314266	0.002104	Prob > F
C. Total	119	2.1831668		<.0001*

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Breaker	4	4	1.0205408	121.2690	<.0001*
Fluid	1	1	0.9188094	436.7218	<.0001*
Fluid*Breaker	4	4	0.5123674	60.8837	<.0001*

Tukey-Kramer:
- No enzyme same as APS
- Cross-effect of APS with fluids same a as G+M with guar, M with guar

Results & Conclusions

- Ammonium persulfate is able to effectively decrease the viscosity and degrade the polymer over time. The proposed enzymes show promise in competing, but do fall short:
  - Galactosidase alone performs poorly as a breaker.
  - Mannanase alone does not perform well enough.
  - Galactosidase and mannanase are the best alternative. Mannanase appears to be most contributing to mixture.
- Enzymes are better at degrading polymer structure, but do not decrease viscosity enough. A breaker must do both.
- Time and concentration do not have statistically-significant effects. Break times are small and breakers are catalytic.
- Fluid, breaker, and cross of fluid and breaker have effects.
- Ammonium persulfate is hazardous; enzymes are not. However, enzymes (especially G+M) can be more expensive.

Future Work

- Perform tests with better engineered enzymes. These can increase thermostability, selectivity, activity – but also cost.
- Fracking wells can vary in temperature and pressure. Test at a range of temperatures (25-75°C) and pressures (1+ bar).
- Focus primarily on G+M as a breaker on short time-scales. May attempt to vary concentration (if no effect, then go lower).
- Supplement ammonium persulfate with enzyme – or simply determine how much APS concentration can be reduced.

Acknowledgements

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References:

•MSDS Search & Product Safety Center. *Sigma-Aldrich*.
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•Cheng, Yu and Robert Prud'homme. "Enzymatic Degradation of Guar and Substituted Guar Galactomannans."